CASE GS -- PP321 STUDY 1 PM --

CHEM -- PP321

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BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

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Bharti, H., D.W. Bewick, and R.D. White. 1985. PP563 and PP321: Degradation in soil. RJ 0382B. ICI Americas Inc., Wilmington, DE. Reference 4J.

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CONCLUSIONS:

Metabolism - Anaerobic Aquatic
Metabolism - Anaerobic Soil

This report is unacceptable for fulfilling guideline requirements for anaerobic aquatic metabolism data because the soil was not flooded for 30 days before the addition of test material.
The report is unacceptable for fulfilling quideline requirements for anaerobic soil metabolism because it appears that anaerobic conditions may not have been achieved after the 30 day period of aerobic incubation. Evidence of this is suggested by the continued evolution of carbon dioxide in the anaerobic soil metabolism study under flooded conditions while little carbon dioxide was evolved when treated soils were flooded immediately without an aerobic incubation period. This study may be accepted if the registrant can show that anaerobic conditions were present under flooded conditions or can otherwise explain the continued evolution of carbon dioxide. A estimate of half-life under anaerobic conditions should also be provided.
No data were provided on the "alcohol" portion of the test substance. These data must be either submitted or specifically referenced.

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MATERIALS AND METHODS:

Cyclopropane-labeled [^{14}C]PP563 (containing "A" and "B" isomers) was applied at 100 or 500 g ai/ha to "pots" (25-g soil; 3.8-cm diameter x 3-cm depth) of sandy loam or loamy sand soil (Tables 1 and 2). Also, the "A" and "B" (PP321) isomers were applied separately at 100 g ai/ha to sandy loam soil. The soils were moistened to 40% of their water-holding capacity at zero suction, except for one set of samples that was flooded immediately after treatment. A second set of samples was flooded after 30 days of aerobic incubation. The treated pots of soil were placed in sealed glass columns through which moistened carbon dioxode-free air was drawn (Figure 1). Air passing over the treated soil was drawn through one tube of 2-methoxyethanol and two tubes of ethanolamine. The soils were incubated at 10 or 20°C for the duration of the study. Soil, water, and trapping solutions were sampled at various intervals up to 181 days posttreatment.

The soils were extracted sequentially with acetonitrile on a wrist action shaker for 30 minutes at room temperature and acetonitrile:water (70:30) by refluxing for 3 hours. Aliquots of the extracts were analyzed for total radioactivity by LSC, and for specific compounds by TLC on silica gel plates developed in hexane:diethyl ether (7:3) or cyclohexane saturated with formic acid:diethyl ether (3:2) and visualized using autoradiography and a TLC linear analyzer. The soil extracts were also analyzed for degradates and specific isomers using GC, HPLC, and MS. The extracted soil was analyzed by LSC following combustion. The water samples were concentrated and analyzed by LSC, TLC, and HPLC. Aliquots of the trapping solution were analyzed for total radioactivity by LSC.

REPORTED RESULTS:

[^{14}C]PP563 (a 60:40 mixture of isomers "A" and "B"), PP321 (isomer "B"), and isomer "A" degraded with an initial half-life between 14 and 30 days posttreatment in aerobic sandy loam soil (Table 3). A second half-life occurred between 30 and 60 days posttreatment for the mixture (PP563) and isomer "A"; isomer "B" did not reach a second half-life until approximately 90 days posttreatment. When the behavior of isomers "A" and "B" in the mixture were examined, both "A" and "B" degraded faster in combination than separately (Table 4). In the mixture, 91.8% of isomer "A" and 85.8% of isomer "B" degraded by 90 days posttreatment, while separately 90.1% of "A" and 78.4% of "B" degraded by 92 days posttreatment (too few samples were obtained to permit these data to be analyzed statistically with any degree of confidence). The "A":"B" mixture also degraded more completely than "A" or "B" alone; by day 90, 58.9% of the applied radioactivity in the mixture had been evolved as $^{14}CO_2$, but only 47.1% of the applied radioactivity was evolved as $^{14}CO_2$ from the soil treated with the "A" isomer alone and only 35.6% was evolved from soil treated with the "B" isomer alone (Table 4). (1RS)-Cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid (up to 7.6% of the applied) and (RS)-α-cyano-3-(4-hydroxy-

phenoxy)benzyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate (up to 12.5% of the applied) were the major nonvolatile degradates in soil treated with PP563, "A" alone, and "B" alone (Table 3).

The "A":"B" mixture (PP563) degraded more slowly under anaerobic (flooded) conditions than under aerobic conditions (Tables 5 and 6). The difference between the "A" and "B" isomer degradation rate was less pronounced under anaerobic conditions; by 131 days posttreatment, 59% of the "A" isomer and 55% of the "B" isomer in the mixture had degraded. PP563 degraded more slowly when applied at 500 g ai/ha compared to 100 g ai/ha, degraded more slowly at 10°C than at 20°C, and degraded more slowly in loamy sand than sandy loam soil (Table 7).

No isomerization of the parent compounds and observed under any conditions during the studies.

DISCUSSION:

1. It appears the anaerobic conditions may not have been achieved under flooded conditions in the anaerobic soil metabolism study. It is noted that very little carbon dioxide was evolved in a study where treated soils were flooded immediately.

2. Studies in which cyclopropane-labeled [^{14}C]PP321 was used provide no information on the fate of the alcohol half of the PP321 molecule in soil. Data on the "alcohol" portion of the molecule should be submitted or specifically referenced.

4. The soil that was used was collected in Berkshire, England and was classified by a method other than the USDA Soil Textural Classification System. The soil was not reclassified.

5. Recovery from fortified samples and detection limits were not reported.

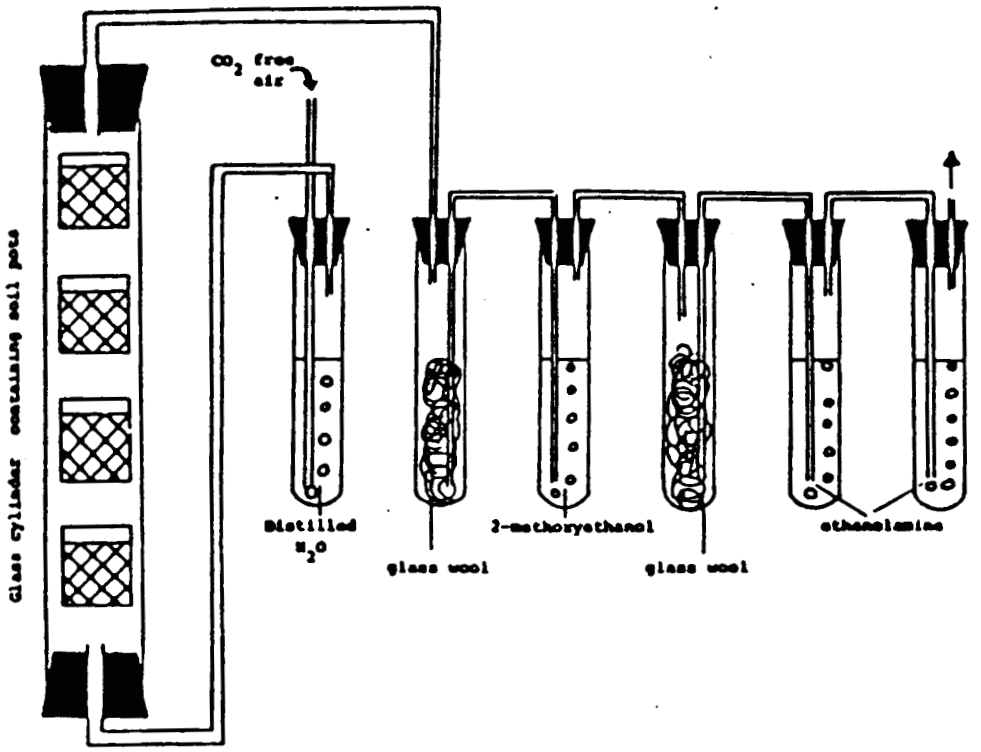

Figure 1. Continuous air-flow incubation apparatus.

Table 1. Test data.

Study	Test substance[a]	Soil type[b]	Incubation conditions		Application rate (g ai/ha)	Sampling intervals (days)
A	PP563	Sandy loam	Aerobic	20°C	100	0 7 14 30 59 90 -- 180
B	PP563	Sandy loam	Flooded after 30 days	20°C	100	-- -- -- -- 60 90 -- --
C	PP563	Sandy loam	Aerobic	20°C	500	0 7 -- 30 -- 90 -- --
D	PP563	Sandy loam	Aerobic	10°C	100	-- 7 -- 30 -- 90 -- --
E	PP563	Sandy loam	Anaerobic (flooded)	20°C	100	0 7 -- 30 59 -- 131 --
F	PP321 ("B" isomers)	Sandy loam	Aerobic	20°C	100	0 -- -- 30 63 92 -- --
G	"A" isomers	Sandy loam	Aerobic	20°C	100	0 -- -- 30 63 92 -- --
H	PP563	Loamy sand	Aerobic	20°C	100	0 7 -- 30 -- 90 -- 181

[a] All compounds were cyclopropane-labeled [^{14}C] material. Refer to Table 2 of this report for isomer ratios.

[b] 18 Acres sandy loam: 28% coarse sand, 33% fine sand, 17% silt, 22% clay, 4.0-4.6% organic matter, pH 6.7, CEC 16.7-19.8 meq/100 g.

Frensham loamy sand: 38% coarse sand, 40% fine sand, 12% silt, 10% clay, 2% organic matter, pH 5.3, CEC 7.2 meq/100 g.

Table 2. Characteristics of the test substance.

Test substance	Total pyrethroid purity (%)[a]	Isomeric composition (%)[b]				
		Cis-isomers				Trans-isomers[c]
		A'	A	B'	B	
PP563	98.0	3.4	57.7	1.8	36.2	0.9
PP321 (isomer pair "B")	98.7	0.1	0.7	2.6	95.1	1.5
Isomer pair "A"	100	1.1	96.5	0.6	1.1	0.7

[a] Determined by TLC; all isomers are included.

[b] These isomers have a cis configuration about the 1,3 bond of the cyclopropane ring:

A'- E(1R, 3R, αR) and E(1S, 3S, αS) enantiomer pair
A - Z(1R, 3R, αR) and Z(1S, 3S, αS) enantiomer pair

B'- E(1R, 3R, αS) and E(1S, 3S, αR) enantiomer pair
B - Z(1R, 3R, αS) and Z(1S, 3S, αR) enantiomer pair

[c] These isomers have a trans configuration about the 1,3 bond of the cyclopropane ring:

C - Z(1R, 3S, αR) and Z(1S, 3R, αS) enantiomer pair
C'- E(1R, 3S, αR) and E(1S, 3R, αS) enantiomer pair

D - Z(1R, 3S, αS) and Z(1S, 3R, αR) enantiomer pair
D'- E(1R, 3S, αS) and E(1S, 3R, αR) enantiomer pair

Sampling interval (days)	Parent[b]	Degradate A[c]	Degradate B[d]	Origin	Other	$^{14}CO_2$	Unextractable
			PP563				
0	95.2	<0.5[e]	<0.5	<0.5	0.9	--	0.1
7	76.3	3.5	3.5	0.9	3.5	3.0	2.3
14	61.7	7.6	7.6	4.4	1.6	8.6	5.7
30	35.2	5.8	11.1	2.8	1.0	24.0	12.0
59	17.9	3.6	7.0	4.0	1.2	46.6	17.6
90	10.1	1.8	3.1	1.3	<0.5	58.9 ✓	18.9
180	5.7	5.7	2.0	<0.5	0.9	70.4	18.7
			PP321 (8 isomers)				
0	98.9	<0.5	<0.5	<0.5	<0.5	--	0.2
30	45.8	6.2	2.5	12.0	2.1	16.1	9.6
63	30.1	5.1	12.5	3.4	0.6	31.8	14.5
92	24.4	6.0	4.2	2.2	<0.5	35.6 ✓	16.8
			A Isomers				
0	97.8	<0.5	<0.5	<0.5	1.4	--	<0.1
30	39.1	5.6	7.5	6.4	0.6	21.9	8.9
63	18.1	3.7	9.1	3.0	<0.5	40.0	15.2
92	10.8	1.2	5.4	0.6	<0.5	47.1 ✓	18.3

[a] CO_2 and unextractable data are from Table 7 in the original document. Characterization of extractables is from Table 8 in the original document.

[b] Distribution of specific isomers is presented in Table 4.

[c] (1RS)-Cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcylopropanecarboxylic acid.

[d] (RS)-α -Cyano-3-(4-hydroxyphenoxy)benzyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.

[e] The detection limit was not specified.

Table 5. Effect of flooding on the distribution of radioactivity (% of the applied) in sandy loam soil treated with cyclopropane-labeled [^{14}C]PP563 at 100 g ai/ha and incubated at 20°C.[a]

Sampling interval (days)	Parent[b]	Degradate A[c]	Degradate B[d]	Origin	Other	$^{14}CO_2$	Unextractable
			Aerobic (40% of WHC)				
0	95.2	<0.5[e]	<0.5	<0.5	0.9	--	0.1
7	76.3	3.5	3.5	0.9	3.5	3.0	2.3
14	61.7	7.6	7.6	4.4	1.6	8.6	5.7
30	35.2	5.8	11.1	2.8	1.0	24.0	12.0
59	17.9	3.6	7.0	4.0	1.2	46.6	17.6
90	10.1	1.8	3.1	1.3	<0.5	58.9	18.9
180	5.7	5.7	2.0	<0.5	0.9	70.4	18.7
			Aerobic for 30 days, then flooded[f]				
30 + 0	35.2	5.8	11.1	2.8	1.0	24.0	12.0
30 + 30	17.7	10.8	6.3	3.2	<0.5	37.3	16.1
30 + 60	13.1	5.3	4.5	1.7	<0.5	45.1	19.7
			Anaerobic (flooded)[f]				
0	93.2	<0.5	<0.5	<0.5	2.0	--	0.1
7	84.7	1.8	0.9	<0.5	1.8	0.2	0.6
30	75.3	10.0	0.8	0.8	0.8	0.3	1.5
59	60.5	22.4	1.4	2.8	0.7	0.4	1.1
131	41.1	34.8	0.6	2.3	2.5	0.5	2.8

[a] CO_2 and unextractable data are from Table 7 in the original document. Characterization of extractables is from Table 8 in the original document.

[b] Distribution of specific isomers is presented in Table 6.

[c] (1RS)-Cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid.

[d] (RS)-α -Cyano-3-(4-hydroxyphenoxy)benzyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.

[e] The detection limit was not specified.

[f] Data include radioactivity in the flood water.

Table 6. Effect of flooding on the distribution of isomers (% of the applied radioactivity) in sandy loam soil treated with cyclopropane-labeled [^{14}C]PP563 at 100 g ai/ha and incubated at 20°C.[a]

Sampling interval (days)	Parent	Cis-isomers				Trans-isomers
		A'	A	B'	B	
		Aerobic (40% of WHC)				
0	95.2	3.2	54.9	1.7	34.5	0.9
7	76.3	2.6	40.9	2.0	29.7	1.1
14	61.7	1.9	31.0	1.6	24.0	1.2
30	35.2	1.0	16.0	1.1	15.1	0.5
59	17.9	<0.5[b]	7.5	0.6	8.0	<0.5
90	10.1	<0.5	4.5	<0.5	4.9	<0.5
180	5.7	<0.5	2.4	<0.5	2.8	<0.5
		Aerobic for 30 days, then flooded[c]				
30 + 0	35.2	1.0	16.0	1.1	15.1	0.5
30 + 30	17.7	0.5	7.5	0.5	7.7	0.6
30 + 60	13.1	0.6	4.7	<0.5	5.7	0.7
		Anaerobic (flooded)[c]				
0	93.2	2.8	53.0	1.8	34.7	0.9
7	84.7	3.2	47.1	1.3	31.8	1.3
30	75.3	2.3	43.0	1.3	27.6	1.1
59	60.5	1.6	30.4	1.4	20.6	1.1
131	41.1	0.7	21.7	0.8	15.5	0.4

[a] Distribution of isomers is from Table 8 in the original document.

[b] The detection limit was not specified.

[c] Data include radioactivity in the flood water.

Table 7. Effect of temperature, application rate, and soil type on the distribution of radioactivity (% of the applied) in sandy loam or loamy sand soil treated with cyclopropane-labeled [^{14}C]PP563 at 100 or 500 g ai/ha and incubated at 40% of moisture holding capacity.

Sampling interval (days)	Parent	Degradate A[b]	Degradate B[c]	Origin	Other	$^{14}CO_2$	Unextractable
		Sandy loam soil, 100 g ai/ha, 20°C					
0	95.2	<0.5[d]	<0.5	<0.5	0.9	--	0.1
7	76.3	3.5	3.5	0.9	3.5	3.0	2.3
14	61.7	7.6	7.6	4.4	1.6	8.6	5.7
30	35.2	5.8	11.1	2.8	1.0	24.0	12.0
59	17.9	3.6	7.0	4.0	1.2	46.6	17.6
90	10.1	1.8	3.1	1.3	<0.5	58.9	18.9
180	5.7	5.7	2.0	<0.5	0.9	70.4	18.7
		Sandy loam soil, 100 g ai/ha, 10°C					
0	95.2	<0.5	<0.5	<0.5	0.9	--	0.1
7	96.5	1.0	1.0	<0.5	2.0	0.2	0.7
30	74.9	5.2	5.2	4.3	<0.5	2.7	4.0
90	28.8	5.5	6.9	3.7	0.9	21.2	14.2
		Sandy loam soil, 500 g ai/ha, 20°C					
0	97.0	<0.5	<0.5	<0.5	2.0	--	0.0
7	87.2	2.8	2.8	<0.5	0.9	1.4	1.2
30	60.5	6.7	4.3	6.7	0.8	11.0	6.8
90	26.4	7.3	4.5	2.0	<0.5	37.0	14.3
		Loamy sand soil, 100 g ai/ha, 20°C					
0	97.5	<0.5	<0.5	<0.5	2.0	--	<0.1
7	94.1	1.9	<0.5	<0.5	<0.5	0.8	0.8
30	72.6	4.0	0.8	0.8	0.8	7.2	6.1
90	46.6	2.7	3.2	4.2	4.2	25.4	12.0
181	21.4	2.2	4.1	8.2	2.5	37.6	14.7

[a] CO_2 and unextractable data are from Table 7 in the original document. Characterization of extractables is from Table 8 in the original document.

[b] (1RS)-Cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcylopropanecarboxylic acid.

[c] (RS)-α -Cyano-3-(4-hydroxyphenoxy)benzyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.

[d] The detection limit was not specified.